The Effect of 1/2 MEV Electron Radiation on the Crystallinity of Graphite Fibers in Composites

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by

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Abstract

Composites of graphite fibers/epoxy and graphite fiber/polyimide have been irradiated with large dosages of 1/2 Mev electrons and examined with x-ray diffraction. Radiation dosages up to 8000 Mrads were applied and no detected differences were observed in the x-ray diffraction patterns of the irradiated and control samples. These results support earlier claims that systems with large numbers of aromatic ring structures are highly resistant to damage from ionizing radiation.

Introduction

Graphite fiber composites are strong, lightweight materials suitable for numerous applications. Examples include structural materials used in the aerospace and trucking industries, in sporting goods and in nuclear reactors. When used in space applications and in nuclear reactors, these materials may be subjected to considerable ionizing radiation dosages over their designed lifetimes. We have reported recently on the effect of 1/2 Mev electrons on the mechanical and morphological properties of graphite fiber/epoxy, graphite fiber/polysulfone and graphite fiber/polyimide composites [1,2]. Radiation dosages as high as 8000 Mrads in the absence of air resulted in a slight increase in the flexural strength and modulus compared to control samples [1,2].

Bullock and coworkers [3-8] have reported several studies of the effects of neutron radiation on the mechanical properties of graphite fibers and graphite fiber/epoxy composites. Irradiation of fibers in the presence of oxygen was shown to cause first an increase in the tensile strengths and then a decrease by as much as 40 percent below the control. Reduction in strength occurred at a more rapid rate when samples were irradiated in air at 75°C than at 140°C, presumably because of a decrease in the production of N_2O_5 above 100°C. They also suggested that oxidation caused surface pitting that resulted in significant strength reduction. However, their work in oxygen-free environments showed that strengths increased with radiation dose. Samples were tested in a gaseous He environment at 175°C and in liquid N_2.

Bullock [8] reported that irradiation of graphite fiber/epoxy composites with neutrons in air at room temperature or at liquid N_2 temperature resulted in a lowering of flexural strengths and moduli in both longitudinal and transverse directions as well as a lowering of horizontal shear strengths. On the other hand, neutron radiation of fibers prior to fabrication into composites resulted in an increase of these properties [6].

Wigner in 1932 first suggested that fast neutrons would displace atoms in the graphite structure [9] resulting in property changes. Numerous studies have since been made showing such changes due to neutron radiation. Simmons [9] published a comprehensive treatment of this work in 1963. Several x-ray diffraction studies have been made of the effects of neutron radiation on the structure. Bacon and Warren [10] published an early review article in which they showed the disruption of crystallites with neutron irradiation. In addition their work suggested that an increase in the c-axis (002) spacing and a contraction in the a-spacing occurred. The perfection of the lattice

could be restored, however, with annealing at high temperatures. Others have reported similar observations.

Jones and Peggs [11-13] have reported that the change in crystallite dimensions due to neutron radiation is highly dependent on the temperature at which irradiation takes place. For example, they obtained not only an increase in the strength and modulus of high modulus graphite fibers irradiated at high temperature, but also an increase in crystallite size, c-axis dimension, and in density. It is likely that this was due to annealing. On the other hand, they obtained a slight decrease in the crystallite size for a higher strength, lower modulus graphite fiber.

The work that we report here is based on an x-ray diffraction study of graphite fiber composites irradiated with large dosages of 1/2 Mev electrons.

Experimental

The x-ray results were taken on a Siemens X-ray diffraction system using $Cu_{k\alpha}$ radiation with a Ni filter. A flat-plate wet-film cassette was used with a 5 cm sample-to-film distance with the fibers perpendicular to the x-ray beam. Diffractometer traces were taken along the equator and the meridian. One set of materials tested was Thornel T300 graphite fiber uniaxially oriented in epoxy(tetraglycidyl 4,4-diaminodyphenyl methane cured with diaminodyphenyl sulfone) hereafter referred to as Narmco 5208. Another set of materials examined was Celion C6000 fiber embedded in a polyimide matrix. The samples were uniaxially oriented with fibers aligned in the long direction. The fibers constituted about 60% of the volume of the composite. Following cure, samples were cut in approximately 2.54 cm widths and were ca. 0.6mm in thickness. The samples were prepared for the radiation treatment by pre-vacuuming for approximately 1 week or longer in a heated vacuum desiccator at

80°C followed by enclosing the samples in aluminum foil and sealing the edges of the aluminum foil with a fast-curing epoxy. A glass tube was inserted to remove gases that had diffused into the system and the material was further vacuumed for an additional week and then sealed.

The samples then were irradiated in an electron accelerator designed for rapid free-radical polymerization of coatings on materials. A conveyor transported the samples in front of the stationary electron beam. The samples passed through the beam twice during each revolution around the conveyor with the beam striking the front and back sides of the samples with approximately one minute between exposure on front and back.

In an earlier study, we reported on the approximate profile of radiation through the thickness of samples of the dimensions used here [1]. Each revolution around the accelerator resulted in a radiation dosage of approximately 10 Mrads. A high percentage of the electrons penetrated through the entire thickness. The approximate temperature rise during exposure was on the order of 50°C above room temperature because the 5 Mrads exposure on each pass was essentially adiabatic. The system would approximately equilibrate to room temperature before being returned to the electron beam. Dosages up to 8000 Mrads were given to the specimens. The x-ray diffraction measurements were made at several dose levels.

Results and Discussion

X-ray diffraction patterns for a control sample and for an 8000 Mrad treated sample of T300/5208 are shown in Figures 1 and 2, respectively. The most intense reflection in the x-ray pattern is the (002) reflection. There is no discernible difference in the x-ray patterns for control and exposed samples. In Figures 3 and 4 are diffractometer traces along the equator and

meridian, respectively, of the control and 8000 Mrad treated samples. The diffractometer traces are identical. There is no difference in the line width of the most intense reflection(002) as a function of radiation dosage. Results for composites subjected to intermediate radiation dosages also gave the same pattern as the control. Additionally, irradiated T300 fibers also showed the same patterns as unirradiated fibers.

In Figures 5 and 6 are diffractometer traces along the equator and meridian for C6000/polyimide composites. Again, there is no difference in the x-ray pattern of a control and a highly irradiated sample (5000 Mrad.) The line width and 2θ value of the (002) reflection are exactly the same.

These results indicate that 1/2 Mev electrons do not significantly disrupt the crystal structure of graphite fibers. The energy is dissipated by ionization and it appears that graphite is particularly resistant to structural changes. Parkinson and Sisman [14] have noted that compounds characterized by the resonance stabilized aromatic ring apparently can absorb and dissipate excitation energy by a process which does not disrupt the molecule. The results reported here confirm that conclusion for graphite fiber exposed to 1/2 Mev electrons.

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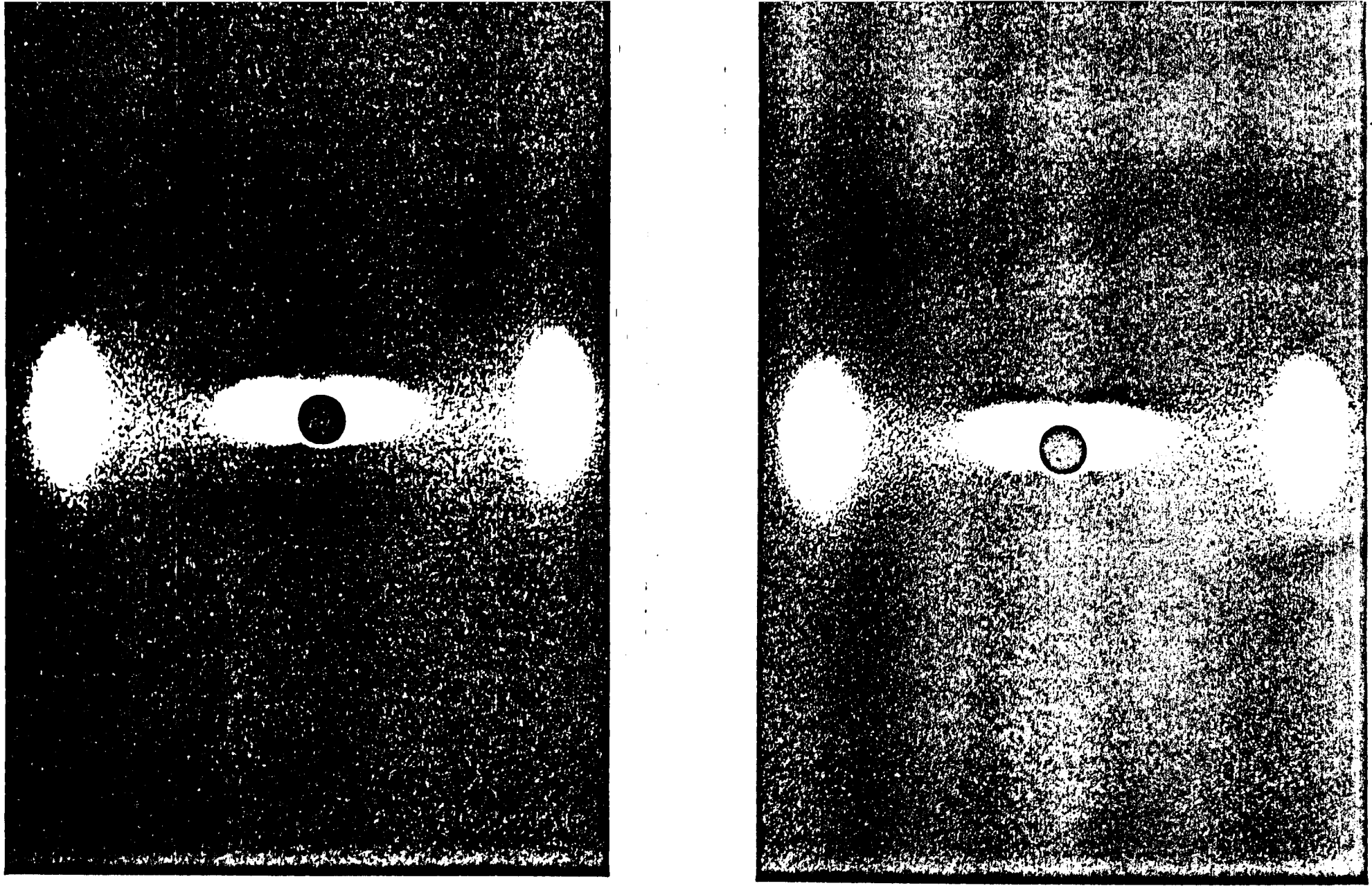
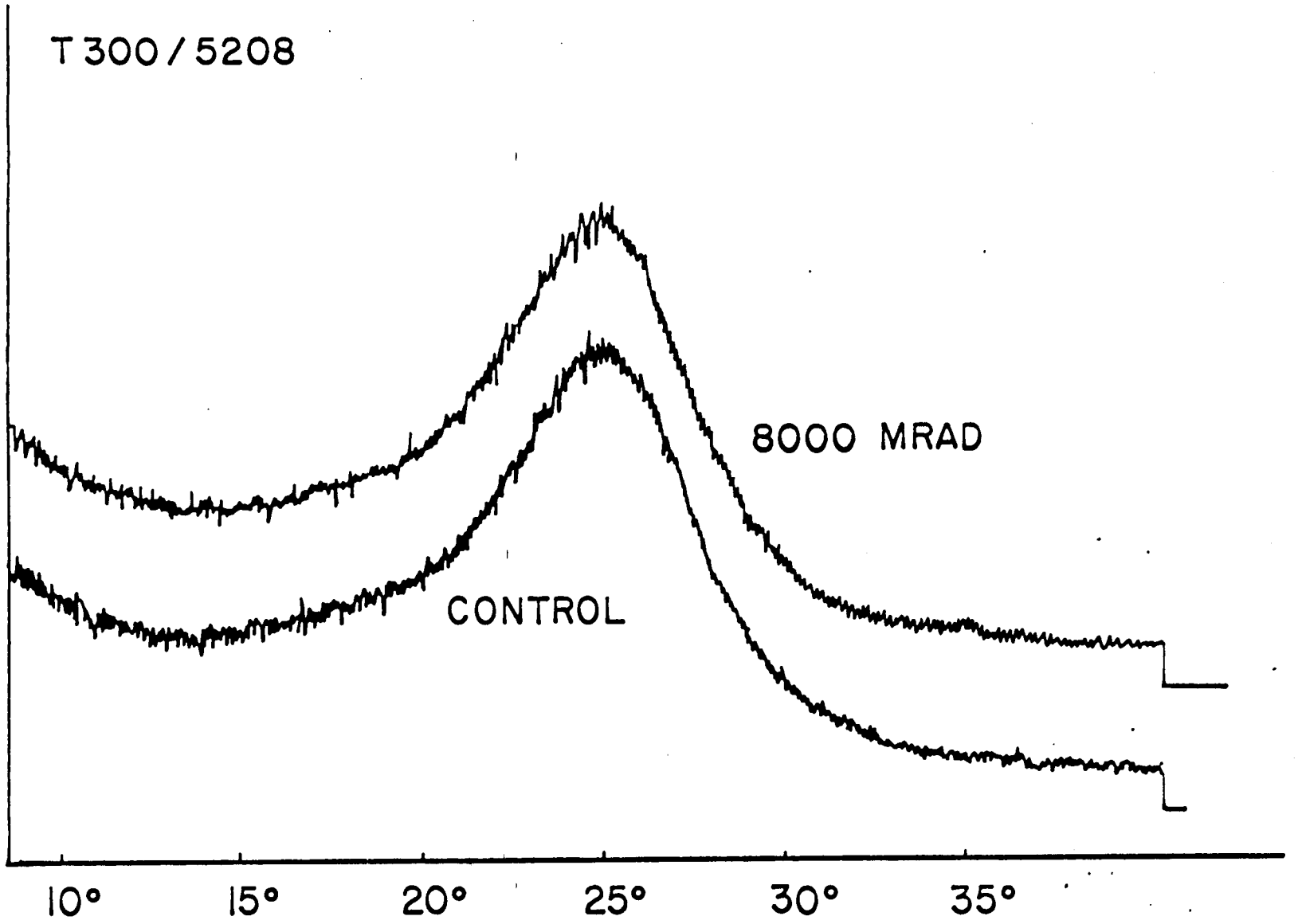


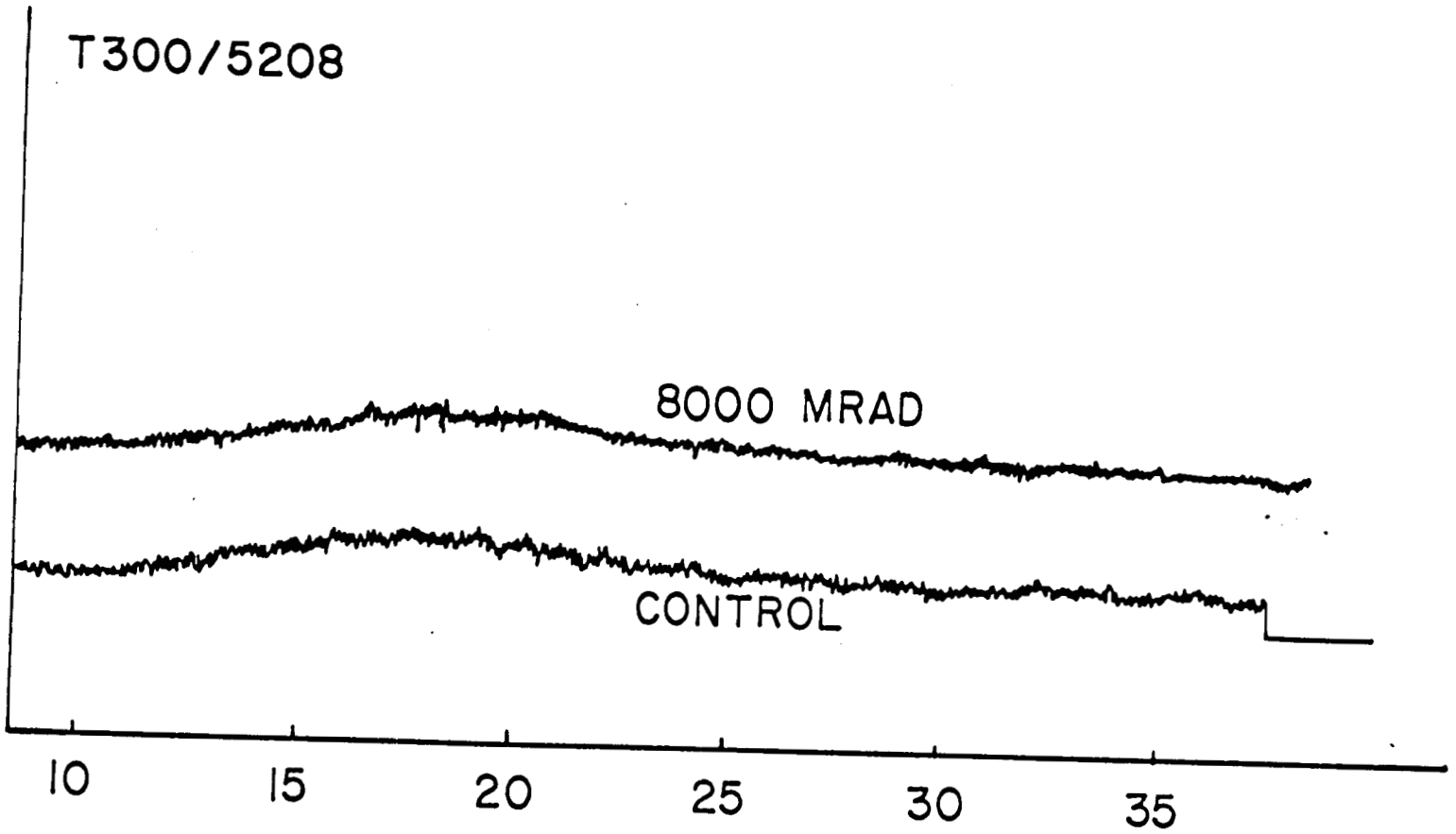
A. Control

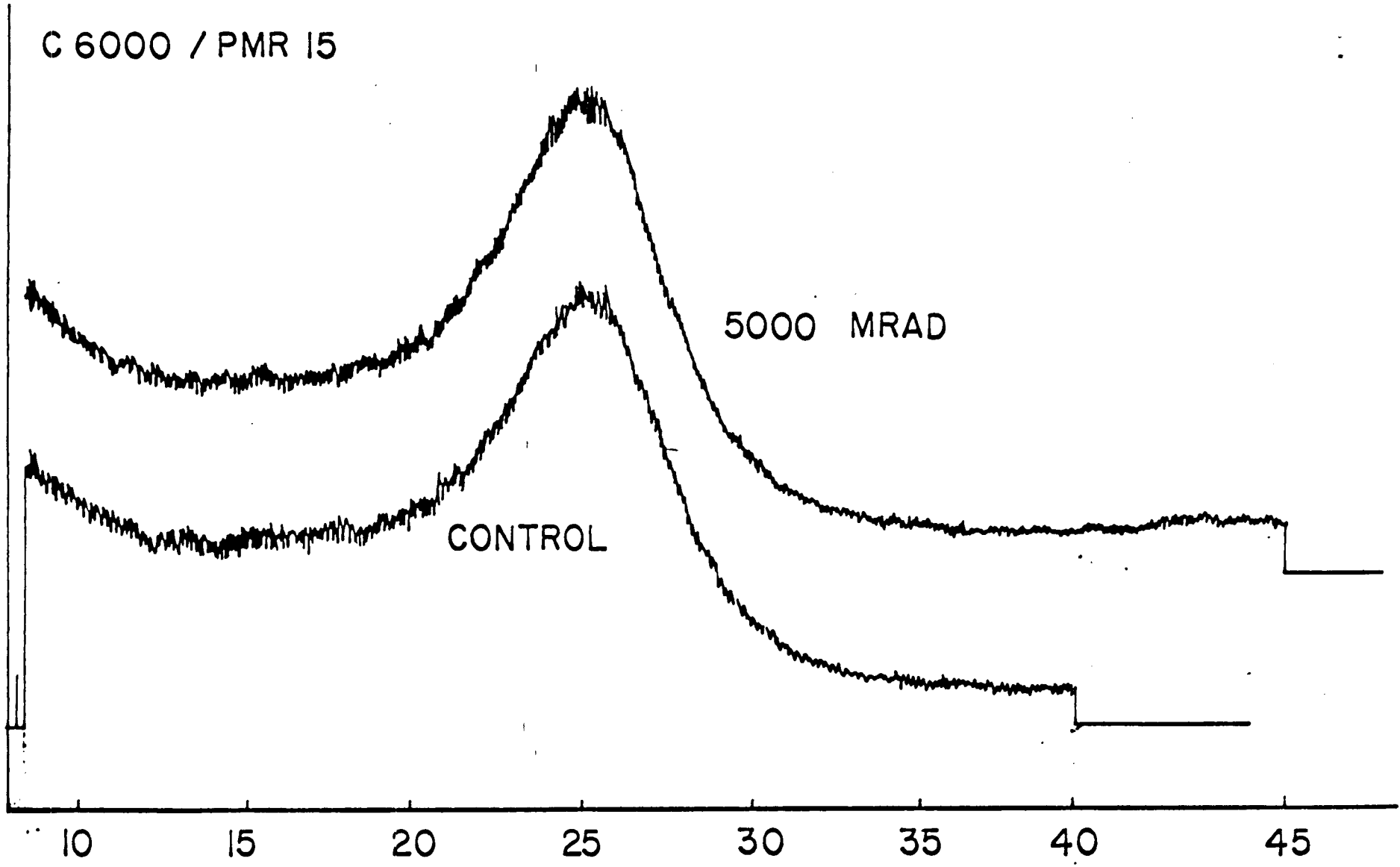
B. 8000 Mrad of 1/2 Mev electrons

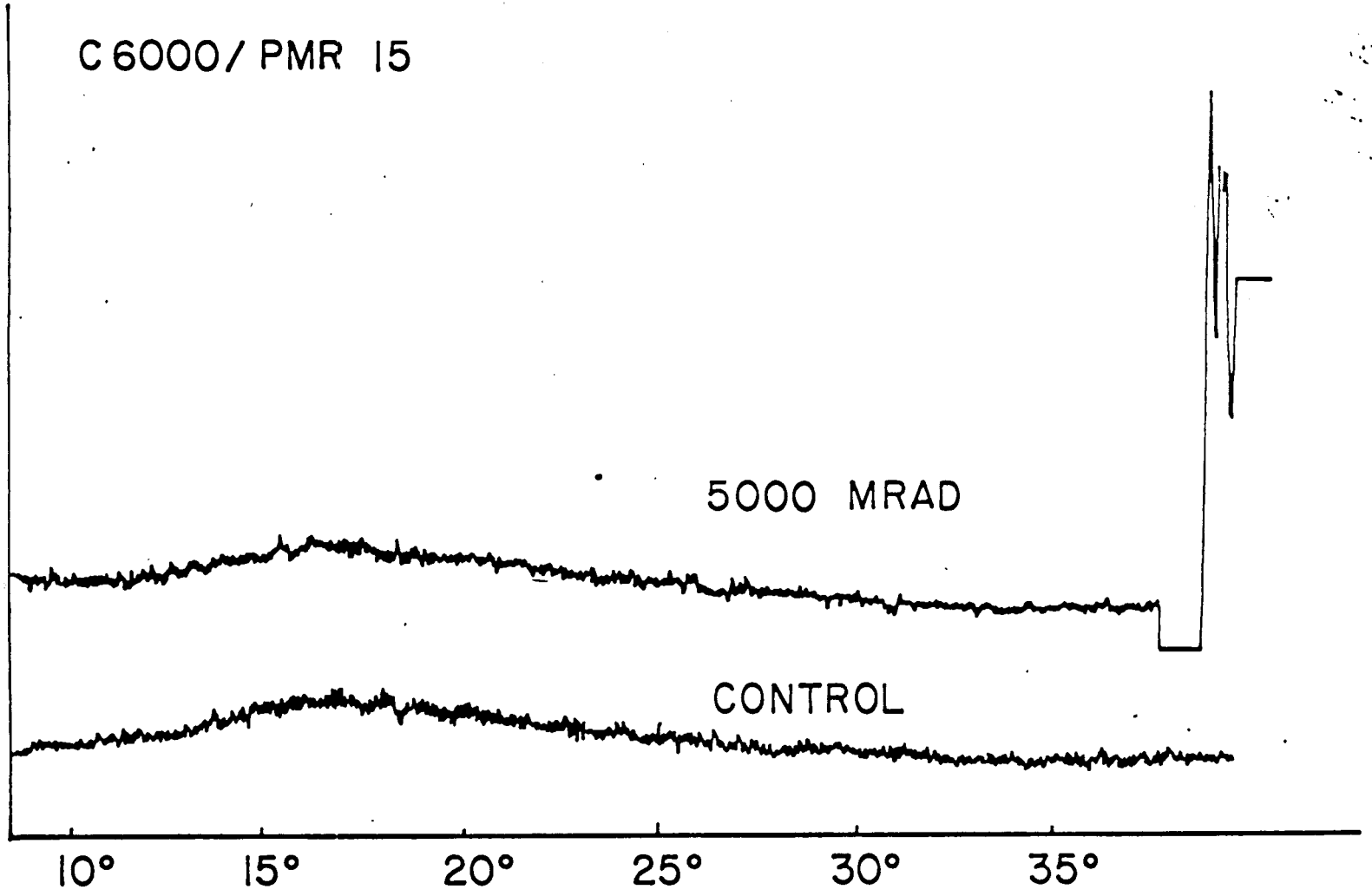
Figure 9

X-Ray Diffraction Pattern of Uniaxial Graphite Fiber Composite (T300/5208)


T300/5208
8000 MRAD
CONTROL
10°
15°
20°
25°
30°
35°


T300/5208
8000 MRAD
CONTROL
10
15
20
25
30
35


C 6000 / PMR 15
5000 MRAD
CONTROL
10
15
20
25
30
35
40
45


C 6000/ PMR 15
5000 MRAD
CONTROL
10°
15°
20°
25°
30°
35°